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Atomic many-body effects for the p-shell photoelectron spectra of transition metals

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Bagus *et al.* Reply: The comment by Taguchi *et al.* [1] on our Letter [2] about the importance of atomic contributions to the $2p$ and $3p$ x-ray photoelectron spectra (XPS) of ionic transition metal materials claims that we have “made serious misconceptions on” their calculations [3,4]. They also criticize our work because we have not used empirical parameters to improve our agreement with experiment. We disagree with their criticisms.

We [2] referred to the work of Kotani and collaborators [3,4] to cite earlier, related work and to place our new work in context. For the most part, our citation of Refs. [3] and [4] is correct. In their Comment [1], Taguchi *et al.* state that they have included angular momentum (AM) recoupling effects in their calculations [3,4]. This is a correct statement, but it does not address our important concern which was not with their calculations but with whether their analysis [4] identified the physical mechanisms for the distribution of XPS intensity into satellites. In our Letter, we distinguish between intershell and intrashell AM coupling and recoupling, and we point out that different mechanisms lead to XPS intensity in the two cases. In their papers [3,4] and Comment [1], the authors do not distinguish between intershell AM coupling and intrashell AM recoupling. Our statement [2] that Ref. [4] did not point out (or “recognize”) the specific role of d subshell AM recoupling is correct.

Taguchi *et al.* [1] complain that we misunderstood their assignment of the second and fourth satellites of the Mn $2p$ XPS. In our Letter [2], we stated that these features were assigned as arising from the mixing of d^5 with charge transfer (CT) $d^6\bar{L}$ and $d^7\bar{L}^2$ configurations. This is correct. In their initial analysis, Okada and Kotani [3] “disregard the multiplet splitting for awhile and analyze the $2p$ -XPS with the bases of d^n and $d^{n+1}\bar{L}$ configurations.” For several Mn compounds, they report, in Table I of [3], the relative energies and intensities of the $2p$ peaks and state that observed values are “well reproduced” with this pure CT model. Later in Ref. [3], a model which also includes atomic “multiplet splittings” is used. However, even then the $2p$ XPS spectra are discussed in terms of the mixing of CT configurations; e.g., see the caption to Fig. 2 of [3]. Taguchi *et al.* [4] report an extension of this CT model [3] such that for Mn compounds “The final states are given by linear combinations of $2p^53d^5$, $2p^53d^6\bar{L}$, and $2p^53d^7\bar{L}^2$ configurations.” They [4] report better agreement with experiment and state that “the third ($3d^7\bar{L}^2$) configuration mainly contributes so as to improve the satellite structure.” These and other remarks in [3] and [4] show that our statement is correct. Our Letter [2] also stated that Taguchi *et al.* [4] had assigned the first $3p$ XPS satellite as a CT high spin multiplet, and the Comment [1] objects to this. Taguchi *et al.* [4] do not appear to make a specific comment about the origin of the ~ 3 eV satellite. In this one case, we have not correctly cited the results of [4]; we apologize for this error.

In their Comment [1], Taguchi *et al.* remark that “atomic multiplet structures” are mainly responsible for much of the satellite structure of the $2p$ and $3p$ XPS. Provided a definition of multiplet structure that includes all possible AM coupling and recoupling is used, we are pleased to agree. Our Letter [2] was primarily concerned with identifying the nature and consequences of these atomic effects. However, Taguchi *et al.* [1] also claim that the CT effect is “still important” for MnO presumably because by switching the CT effect on “the agreement with the experimental results is improved.” Furthermore, they [1] claim that the effects of a reduction of Slater integrals and a term-dependent core hole lifetime are also “important to obtain a better agreement with the experimental results.” We are criticized [1] for not having used these empirical parameters to improve our agreement with experiment. We reject this criticism. The value of adjusting empirical parameters to reproduce known data is limited. For example, the reduction of the Slater integrals is simply a way of introducing electron correlation effects that are not included in their model Hamiltonian. However, it is not known whether this empirical treatment describes interatomic or intra-atomic correlation effects. This important distinction can be made with rigorous, nonempirical, *ab initio* treatments, and our objective was to use this theory to identify the physical mechanism responsible for the observed spectra. A special value of *ab initio* treatments is that they provide benchmarks for semiempirical studies.

In summary, our citation [2] of Refs. [3] and [4] is, in substance, correct and fair. We are pleased that Taguchi *et al.* [1] appear to have shifted toward our conclusion [2] that atomic many body and relativistic effects account for most of the features of the MnO $2p$ and $3p$ XPS spectra. We hope that our ongoing rigorous, nonempirical theoretical work will identify the mechanism needed to remove the remaining disagreements with experiment.

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